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# PRELIMINARY TEST OF THE WET OXIDATION OF ORGANICS IN BASIN F WASTEWATER
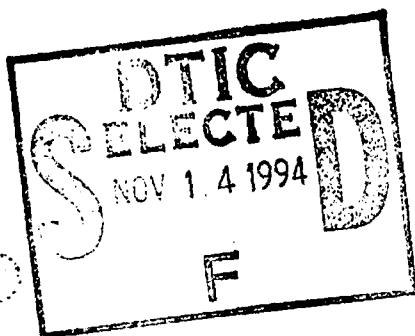
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## ROCKY MOUNTAIN ARSENAL

Supporting Program Under ITARMS 1.05.7

By

Contamination Control Directorate

Rocky Mountain Arsenal
Commerce City, Colorado 80022

REPORT NO. I

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VARIOUS DECONTAMINATION PROCESSES ARE CANDIDATE FOR TREATMENT OF WASTEWATER FROM SEVERAL SOURCES AT RMA. WET OXIDATION IS A UNIT OPERATION THAT INVOLVES OXIDATION OF ORGANIC MATERIALS WITH GASEOUS OXYGEN IN THE PRESENCE OF LIQUID WATER AT TEMPERATURES BETWEEN ABOUT 400 DEGREE AND 700 DEGREE F. WASTE FROM BASIN F AT RMA HAS SEVERAL PERCENT ORGANICS CONTENT. IT WAS USED FOR THE INITIAL WET OXIDATION EXPERIMENT BECAUSE THE WET OXIDATION RATE IS PROPORTIONAL TO THE CONCENTRATION OF ORGANICS. THE EXTENT OF OXIDATION OBTAINED IN THIS FIRST TRIAL WAS ABOUT 78 PERCENT OF THE BASIN F COD IN 60 MINUTES (74 PERCENT IN 30 MINUTES).

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SUMMARY:

Various decontamination processes are candidates for treatment of waste-water from several sources at Rocky Mountain Arsenal (RMA). Because of differences among sources, the processes will consist of several chemical unit operations in combination. Wet oxidation is a unit operation that involves oxidation of organic materials with gaseous oxygen in the presence of liquid water at temperatures between about 400°F and 700°F. Pressures required increase with temperature; in order to maintain the water in its liquid state, at 550°F the pressure if 1,500 PSIG. Pressure in excess of the vapor pressure of water is a requirement due to the partial pressure of air and of some organics.

Waste from Basin F at RMA has several percent organics content. It was used for the initial wet oxidation experiment because the wet oxidation rate is proportional to the concentration of organics. Other sources may be found to have sufficient organics concentration to be suitable, after the optimum reaction conditions have eventually been established:

The extent of oxidation obtained in this first trial was about 78 percent of the Basin F COD in 60 minutes (74 percent in 30 minutes). The result is encouraging but a preliminary economic estimate should be made to see if further study of the wet oxidation process can be justified.

INTRODUCTION:

Basin F at RMA has been a holding basin for waste streams from all chemical manufaturing operations since its construction in the early 1950's. For a complete analysis of both the liquid and sediments see Reference 1.

. The most objectionable features of Basin F are:

(1)  The Basin's potential for leaking and thus contaminating an aquifer that underlies the Basin; water in the aquifer flows generally north toward the boundary of RMA.

(2)  The Basin's potential for flooding.  An earthen dike retains approximately 800 acre feet of wastewater in an area with a history of moderate earthquakes.

(3)  The Basin is a source of objectionable odors and of undefined volatile organic compounds.

Methods for future management of this Basin will depend on the degree of success shown by the individual treatment processes that are eventually developed, as measured by their effectiveness and their cost.  Such treatment processes can also be expected to be applicable to the industrial waste streams currently entering the Basin and to waste streams from other less contaminated sources at RMA.  Reference 2 outlines the general research/development strategy involved, although there are modifications suitable to particular waste stream sources. In general, the ideal process would be to remove organics completely and then treat the organic-free aqueous as economically as possible so that it will meet Colorado water standards.  In this context, "economics" is intended to reflect the capital, material, and operating costs necessary to procude a water stream that will continue to be acceptable to Colorado for that period of time necessary to eliminate the contamination.

As one element of a possible decontamination process, a preliminary evaluation of a chemical unit process called wet oxidation has been conducted.  The process was tested because of the following advantages:

/ (1)  Air is the least expensive oxidant available, unless other costs such as heating and compression become prohibitive.  It is particularly suitable for first-stage treatment of waste source containing high organic levels.

/ (2)  Iron and manganese are precipitated under wet oxidation reaction conditions.

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(3)  Residual oxidant is harmless so that any desirable excess can be used.

Some disadvantages should also be recognized:

(1)  Temperatures between about 450°F and 700°F and correspondingly high pressures lead to requirements for heavy walled vessels and high pressure pumps.

(2)  Wet oxidation tends to produce oxygenated organic compounds of low molecular weight.  These compounds tend to be least adsorbed by activated carbon; polishing operations designed to remove the last traces of organics may be affected.

(3)  Corrosion prevention increases equipment costs.

As an estimate, the present state of the art can provide an acceptable compromise between the above advantages and disadvantages, probably for sources which have high organic levels.

Preliminary tests of the wet oxidation process were conducted (gratis) by Astro Metallurgical Corporation (AMC), Wooster, Ohio.  Waste water from Basin F was tested and analyzed; some additional analyses were conducted at Rocky Mountain Arsenal (RMA).

EXPERIMENTAL:

The initial test was conducted at 550°F and 1500 PSIG; six samples were taken over a period of two hours.

Analyses by AMC consisted of total oxidizable carbon (TOC), Chemical Oxygen Demand (COD), and total solids.  Total solids is a measurement that involves evaporation of a weighed sample; it includes non-combustibles as well as oxidizable or combustible organics.

In addition to the AMC analyses, the RMA MALD laboratory measured iron and DIMP levels in the samples and also provided gas chromatograph scans.

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TABLE I

RAW MATERIAL (BASIN F) PROPERTIES

pH          = 7.4              Conductivity = 40,000 umhos
Chlorides   = 50,000 mg/l      Dissolved $O_2$ = <1 mg/l
Iron        = 5 mg/l           Alkalinity + 700 mg/l
Total Solids = 169,838 mg/l

TABLE II

ANALYSES RECEIVED FROM ASTRO METALLURGICAL CORP.

| MINUTES | TOC | | COD | | TOTAL SOLIDS | | PH |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | PPM | % REMOVED | PPM | % REMOVED | % W | % REMOVED | |
| 0 | 13,365 | 0.0 | 27,325 | 0.0 | 16.98 | 0.0 | 7.25 |
| 3 | 4,615 | 65.5 | 12,811 | 53.1 | 13.66 | 19.55 | 9.31 |
| 6 | 4,144 | 69.0 | 10,216 | 62.6 | --- | --- | 9.26 |
| 12 | 2,532 | 81.1 | 7,586 | 72.2 | 11.80 | 30,51 | 9.25 |
| 30 | 2,515 | 81.2 | 6,989 | 74.4 | 8.65 | 49.06 | 9.29 |
| 60 | 2,270 | 83.0 | 5,972 | 78.2 | --- | --- | 9.26 |

Wet oxidation at 550°F and 1500 PSIG gave the above results. Effects of higher temperatures, pH, and catalysts remain to be measured. COD and TOC differences reflect the two different oxidation procedures involved. The above data is presented graphically in Figure I.

TABLE III

ANALYSES CONDUCTED BY MALD AT RMA

| Minutes | DIMP | IRON | ALDRIN | DIELDRIN |
| --- | --- | --- | --- | --- |
| | | NOT consistant with actual solutions | | |
| 0 | 390 ug/l | 0.74 ppm | -- | -- |
| 3 | 3.7 | 0.17 ppm | -- | -- |
| 6 | 3.7 | <.1 | -- | -- |
| 12 | 3.2 | <.1 | -- | -- |
| 30 | 3.3 | <.1 | -- | -- |
| 60 | 3.3 | <.1 | <.3 ppb | .5 ppb |

The manganese level in Basin F is only 0.17 ppm and an analysis was therefore not attempted. Iron reduction at zero time (5 to 0.74 ppm) indicates air was

admitted before the sample was drawn; the remaining analyses show a very rapid

oxidation and removal of iron. DIMP concentration is 20 ppm in Basin F but it had

substantially disappeared by the time the first sample could be taken. The 3.7

ug/l levels in the remaining samples are evidently due to analytical interfer-

ences.

In Reference 1, Aldrin and Dieldrin levels for 1975 are, respectively,

1410 and 460 ppb; since manufacturing has ceased, the levels are about 100 ppb.

The levels at 60 mins. in Table III show substantial destruction. As additional

data for the 60 min sample, Isodrin = <.3; DDE = .8; Endrin = <.3, DDT = .6 ppb.

In addition, a gas chromatograph-mass spectrometer scan was conducted. DIMP,

DMMP and TMP (Diisopropylmethylphosphanate, Dimethylmethylphosphonate, and Tri-

methylphosphite were reduced to very low levels within six minutes or less; methyl

sulfone remained unchanged. There was a concurrent appearance of new peaks at

both ends of the chromatograph scan. The more volatile compounds appeared to pass

through a minimum at about 12 minutes and to increase thereafter, presumably as a

result of continued wet oxidation. The less volatile compounds (maximum elution

times measured) also appeared to increase with reaction time. In both cases,

however, more data would be necessary to establish a definite pattern.

The appearance of all samples after six minutes was substantially the same;

after settling, the supernatant liquid was clear with a slight blue tinge due to

copper. A small amount of rust colored sediment was present but in insufficient

amount for analysis. After six minutes the samples were odor-free.

DISCUSSION:

Wet oxidation kinetics are called pseudo first order in chemical terms. The

rate of disappearance of oxidizable organic material is proportional to the con-

centration of organic material present at a given time. The concentration of

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oxygen, above a certain minimum, has no effect on the rate of oxidation; the minimum is expressed in Reference 3 as ($O_2$/COD>0.8) but the units for $O_2$ are not specified (the $O_2$ units should be units of concentration and are presumably atmospheres). There is essentially zero oxidation at oxygen concentrations below the minimum (Page 2-9, Reference 3).

Typically wet oxidation proceeds rapidly through the first two-thirds to three-fourths of the organic material and then suddenly changes to a significantly slower rate of reaction. Large organic molecules are present initially. Their oxidation is rapid but molecules of lower molecular weight are by-products of the oxidation, and these smaller organic molecules are resistant to further oxidation.

The data from Table II appears to represent a typical wet oxidation. The pseudo first-order constants from both COD and TOC analyses have been calculated from a first-order rate equation and listed in Table IV.

TABLE IV

PRELIMINARY ESTIMATES OF THE WET OXIDATION RATE CONSTANT AT 550°F and 1500 PSI

| SAMPLE TIME MIN | $\Delta t$ | C (COD) (PPM) | K * (MIN$^{-1}$) | C (TOC) (PPM) | K * (MIN$^{-1}$) |
|---|---|---|---|---|---|
| 0 | 0 | 27,325 | --- | 13,365 | --- |
| 3 | 3 | 12,811 | .110 | 4,615 | .154 |
| 6 | 3 | 10,216 | .030 | 4,144 | .0156 |
| 12 | 6 | 7,586 | .020 | 2,532 | .0357 |
| 30 | 18 | 6,989 | .002 | 2,515 | .0004 |
| 60 | 30 | 5,972 | .002 | 2,270 | .0015 |

A) Oxidize to 5 ppm COD $\Delta t = \left(\log \dfrac{(5972)}{(\ 5\ )}\right) \Big/ .002 = 1398$ MIN = 23 hours

B) Oxidize to 273 ppm COD (99%); $\Delta t = 669$ MIN = 10 hours

*K = $(\log C_1/C_2)\big/(t_2-t_1)$; K$^1$ is from TOC data

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Although the wet oxidation times were not chosen for accurate measure of the slow rate constants, the second, slower oxidation appears to be (very roughly) 1/30 as fast as the initial oxidation rate. As an estimate based on the slower oxidation rate, it would take about eleven hours to oxidize 99% of the organic material and about twenty-four hours for 99.98% oxidation, which would leave a COD of 5. As a practical matter, this estimate has a very large uncertainity (easily as much as ±75% of its apparent value) because of the limited experimental basis and because the chemistry might undergo further rate changes during a longer reaction.

From Table III, DIMP disappears during the first 10 or 20 percent of the COD reduction. Contrary to our experience with carbon adsorbtion, DIMP is not an effective measure of organic removal during wet oxidation.

Iron removal is extremely rapid and the same could be expected for manganese, for sources where it is present. Manganese removal is pH-sensitive and approaches 100% at pH 9.4 or above. Table II shows essentially this pH throughout the oxidation. Where necessary, small pH adjustments could be made.

Total solids (Table II) consists of both the organic and inorganic substances present. The reduction in total solids is due to oxidation of the organic portions. The reduction reached 49% at the thirty minute period; the 60 minute COD indicates that some further reduction of total solids probably occurred. The inorganic solids cannot be removed by oxidation so that total solids removal by oxidation probably cannot exceed about 50% of the original quantity.

The appearance of volatile compounds in the chromatograph analyses, described above, corresponds to the known tendency for materials of lower molecular weights to accumulate toward the latter part of a wet oxidation reaction. The heavy ends (peaks at longer retention times on the chromatograph) may be fractions of molecules that were too heavy to get through the chromatograph column at all, prior to

the wet oxidation. A complete explanation of light ends composition and formation rates is probably unnecessary as far as process development is concerned.

## CONCLUSIONS:

(1) The oxidation potential of the wet oxidation procedure is high enough to destroy a large part of the organic contaminants present in Basin F. The initial results obtained indicate that use of increased temperatures, catalysts, and possibly other parameters could lead to perhaps 90% oxidation of organics from concentrated sources such as Basin F, but the kinetics indicate that some low but significant concentration of organics would remain in the output from any economically sized plant. The measurement and identification of these residual organics would be one objective for further experiments; a second objective would be the definition of the relationship between the organics concentration and the cost of its reduction via wet oxidation.

(2) In conjunction with further wet oxidation experiments, it is important to develop a preliminary measure of the range to be expected for the wet oxidation costs that correspond to a particular final concentration of organics. This will provide some definition of the best place in the wastewater treatment process at RMA for wet oxidation.

(3) The wet oxidation test results reported here are very encouraging, but they are the first such data on RMA wastewater. Many variations of the procedure are known and considerable improvement of the process is to be expected from further experimentation.

## PLANS FOR THIRD AND FOURTH QUARTERS FY 78:

During the third and fourth quarters of FY 78 reasonable performance expectations will be outlined from a further investigation of the wet oxidation reaction variables. According to the literature, the oxidation rate can be affected by six or eight variables; the most important of these will be

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selected from a partial factorial experimental design. An estimate of optimum performance will be developed from a few additional experiments, if necessary. The dependent variables of primary interest are reaction time and the COD or TOC of the effluent; other effluent characteristics of interest will be the composition of insolubles formed and the nature of the remaining organics and inorganics in the effluent. A biological test of effluent toxicity would be a reasonable way to decide whether or not an evaporation pond would constitute an environmental hazard; limited quantities from batch experiments may force postponement of this test.

Process cost estimates will be developed for comparison of wet oxidation with other process alternatives.

The literature search will be continued as a means to concentrate the experimental work in productive areas.
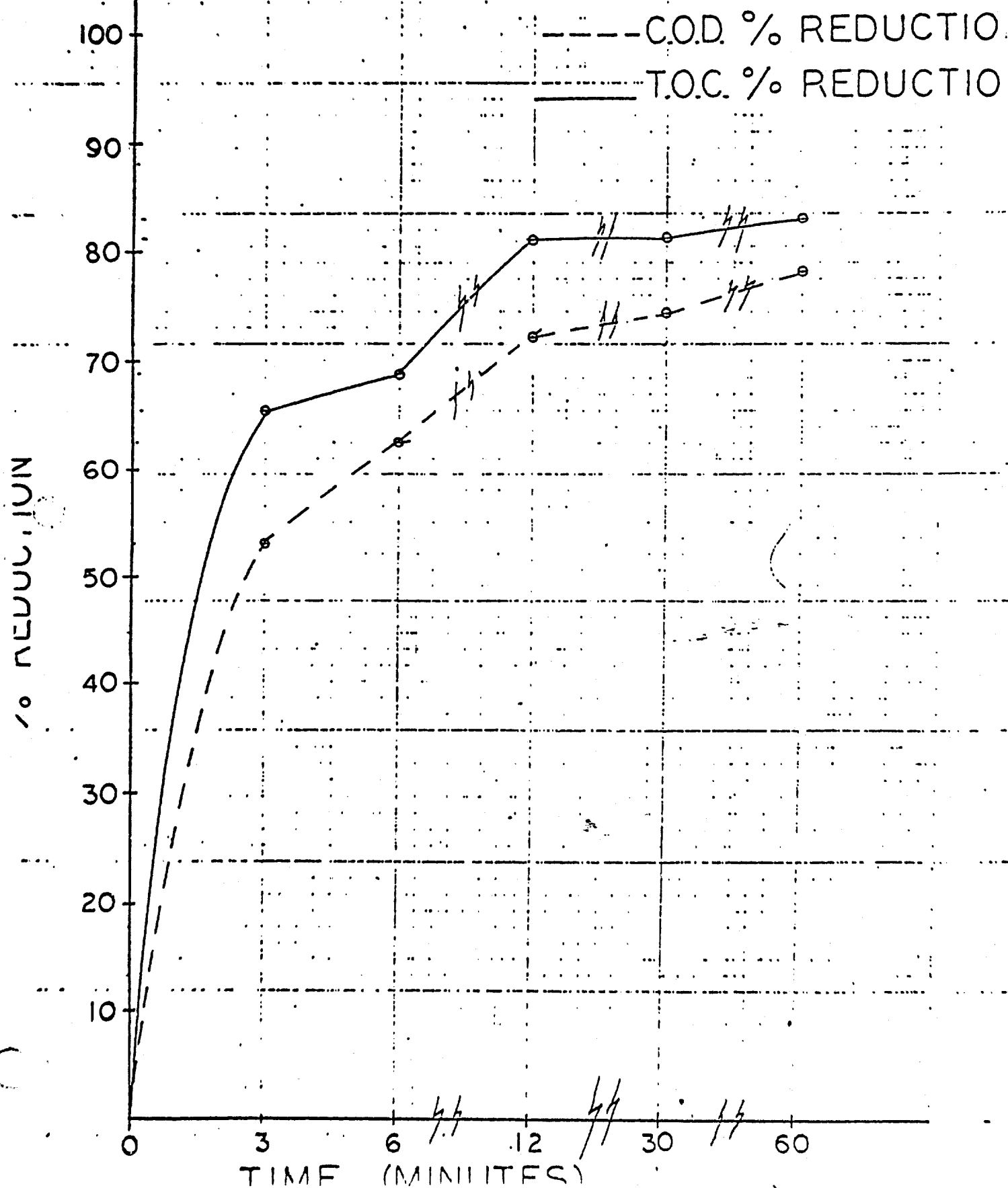
REFERENCES:

Reference (1) - Data attached.

Reference (2) - H. L. Lawless "Proposed Research/Development Strategy for Treatment of Subsurface Waters, Report No. I, 14 Sep 1977.

Reference (3) - D. W. Bridger and W. M. Fassell, "Pilot-Plant Demonstration of Wet Oxidation for Treatment of Shipboard Wastewaters". Final Report for Department of Transportation, United States Coast Guard. Report No. CG-D-34-76 Task No. 4322.2.2 Available from NTIS (ADA 028812).

PERCENT REDUCTION T.O.C. & C.O.D. vs TIME FOR "BASIN F" LIQUOR

FIGURE I

C.O.D. % REDUCTIO
T.O.C. % REDUCTIO

BAS... F ANALYSIS
(PPM, *PPB)

| | DOW 1957 | AEUA 1965 | AEUA 1970 | RMA Files Apr 1970 | RMA Files Jun 1970 | CDH 1970 | AEUA 1973 | CDH 1975 | Intra Search 1976 | MALD & UES 1977 |
|---|---|---|---|---|---|---|---|---|---|---|
| DIMP | | | | | | | | 408 | | |
| DCPD | | | | | | | | 1.58* | | |
| Aldrin | | 66 | | | | 900* | 2,064 | 1,410* | | |
| Alkalinity (Total) | | | | 9,270 | 10,100 | | 3,500 | | | |
| Aluminum | | .46 | | | | | 0.44 | | | |
| Ammonia (as N) | | | | | | | 11 | | | |
| Arsenic | | 0.59 | 1.07 | 0.9 | 1.4 | | 2.70 | 0.45 | 3 | 1.. |
| Boron | | | | | | | 31 | | | |
| Cadmium | | | | | | | 42 | | | |
| Calcium (as CaCO3) | 48.1 | 164 | 120 | 300 | 200 | | 88 | | | 120 |
| Chloride | 6,035 | 5,920 | <25,550 | 24,000 | 26,650 | | 41,278 | 43,000 | | 51,557 |
| Chromium (*3) | | | | | 0.75 | | 0.095 | | | |
| Cobalt | | | | | | | 0.61 | | | |
| COD | | 4,800 | 15,950 | 15,950 | 11,400 | | 230 | 16,000 | | 25,000 |
| Conductivity | | | 64,500 | 60,700 | 59,300 | | 880 | | | |
| Color | | | | | 50,000 | | 120,000 | | | |
| Copper | | | 240 | 204 | 220 | | 155 | 480 | 740 | 800 |
| Cyanide | | | | | | | 300 | | | |
| Dieldrin | | 33 | | | | 639* | 1,748* | 460* | | |
| Endrin | | 47 | | | | | 178.4* | 90* | | 1.5 |
| Fluoride | | 35 | 1,050 | | 2,000 | | 10.5 | 77 | | |
| Hardness | | | 700 | 600 | 900 | | 320 | | | 2,456 |
| Iron | | 2.1 | | | | | 4.24 | | | 6.3 |
| Lead | | | | | | | 42* | | | |

(Continued)

BASIN F ANALYSIS (Concluded)
(Flow, #TTU)

| | DOW 1957 | AEHA 1965 | AEHA 1970 | RHA Files Apr 1970 | RHA Files Jun 1970 | CDH 1970 | AEHA 1973 | CDH 1975 | Intra Search 1976 | HALD & WES 1977 |
|---|---|---|---|---|---|---|---|---|---|---|
| Magnesium | 12.2 | 280 | 73 | 73 | 170 | | 24.3 | | | 38 |
| Manganese | | | | | | | 0.17 | | | 0.68 |
| Mercury | | | | | | | 3.0* | | 100* | 27* |
| Nickel | | | | | | | | | | 5.6 |
| Nitrogen (Nitrate & Nitrite) | | | | | | | | | | 133 |
| Nitrate | | | | 8.6 | 8.7 | | 8.7 | | | |
| Nitrite | | | | 0.80 | 0.28 | | 0.23 | | | |
| pH | 7.6 | 8.2 | 8.6 | | | | 7.38 | 5.1 | | 7.0> |
| Phenolic | | | 0.8 | | | | 0.290 | | | |
| Phosphorous (as P) | | 930 | 340 | 246 | 370 | | 380 | | | |
| Phosphorous (as O-PO$_4$) | | | 110 | 110 | 108 | | | | | 119 |
| Potassium | | | | | | | 13.5 | | | |
| Silica (SiO$_2$) | | | | | | | 8.0 | | | |
| Silver | | | | | | | 0.03 | | 0.06 | |
| Sodium | 4,715.1 | 6,300 | 29,500 | 26,000 | 29,000 | | 9,537† | 27,000 | | 36,400 |
| Dissolved Solids | | | | | | | 156,600 | | | 22,000 |
| Total Organic Carbon | | | | | | | | | | |
| Total Solids | 13,103 | 18,424 | 88,670 | 80,400 | 83,500 | | 182,550 | | | 156,000 |
| Organophosphorous | | | | | | 0 | | 0 | | |
| Bicarbonate | 2,119 | | | | | | | | | |
| Sulfate | 182.5 | | | 9,620 | 13,184 | | | 15,420 | | 24,237 |
| Zinc | | | 15.8 | 26 | 13.5 | | 1.69 | | 1.7 | 1.3 |
| Phenolphthalein Alkalinity | | | 700 | 700 | 570 | | | | | |

† May be a low value

TABLE 2 (Continued)

AEHA 1965

BASIN F Sludge (Mud)[4]

(and two percent protective soil layer - mg/kg

|  | 1965 |
|---|---|
| COD | 47,900 |
| Chlorides | 3.4 |
| Fluorides | 760 |
| Arsenic | 1.59. |
| Phosphorous | 200 |
| Sulfates | 37 |
| Sulfides | 50 |
| Calcium | 8400 |
| Iron | 8700 |
| Aldrin | 55 |
| Dieldrin | 34 |
| Endrin | 34 |
| Parathion | 140 |
| Methylparathion | <.0 |